

**BIOCHEMICAL CONVERSION PROGRAM
ANNUAL REVIEW MEETING**

at the
SOLAR ENERGY RESEARCH INSTITUTE

October 13-15, 1987

B02318 3398
Biofuels Information Center

ACID RECOVERY OF POLYAMINE

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ABSTRACT

Acid hydrolysis of cellulose will result in solutions of glucose and xylose contaminated by the acid. Neutralization with lime will remove most of the sulfuric acid in the form of precipitated gypsum but a sufficient amount of calcium ions will remain in the solution. The calcium ions are inhibitory towards xylose isomerase enzyme which is sometimes employed to convert xylose to xylulose to be fermented to ethanol. Removal of the acid catalysts by a solid resin adsorbent will therefore help to avoid this problem of inhibition. A class of polymers (PA-polyamine) have been used to remove acids from the sugar solution.

This work was partially supported by SERI through a subcontract which was terminated on July 31, 1987. The project is currently carried on with limited Purdue internal support.

ACID RECOVERY ON POLYAMINE

I. INTRODUCTION

A 2-stage acid hydrolysis process was developed at Purdue University. As shown in the flow diagram in Figure 1, a mixture of glucose and xylose will be contaminated by the acid catalyst (sulfuric acid) in the final hydrolyzate. Neutralization with lime will remove most of the sulfuric acid as precipitated gypsum. However, a sufficient amount of calcium ions will remain in the sugar solution.

Xylose can be converted into ethanol if it is first isomerized by xylose isomerase to form xylulose (Gong et al. 1987; and Chiang et al. 1981). A coupled enzymatic isomerization and yeast fermentation will allow us to convert both xylose and glucose into ethanol (Rodriguez 1983).

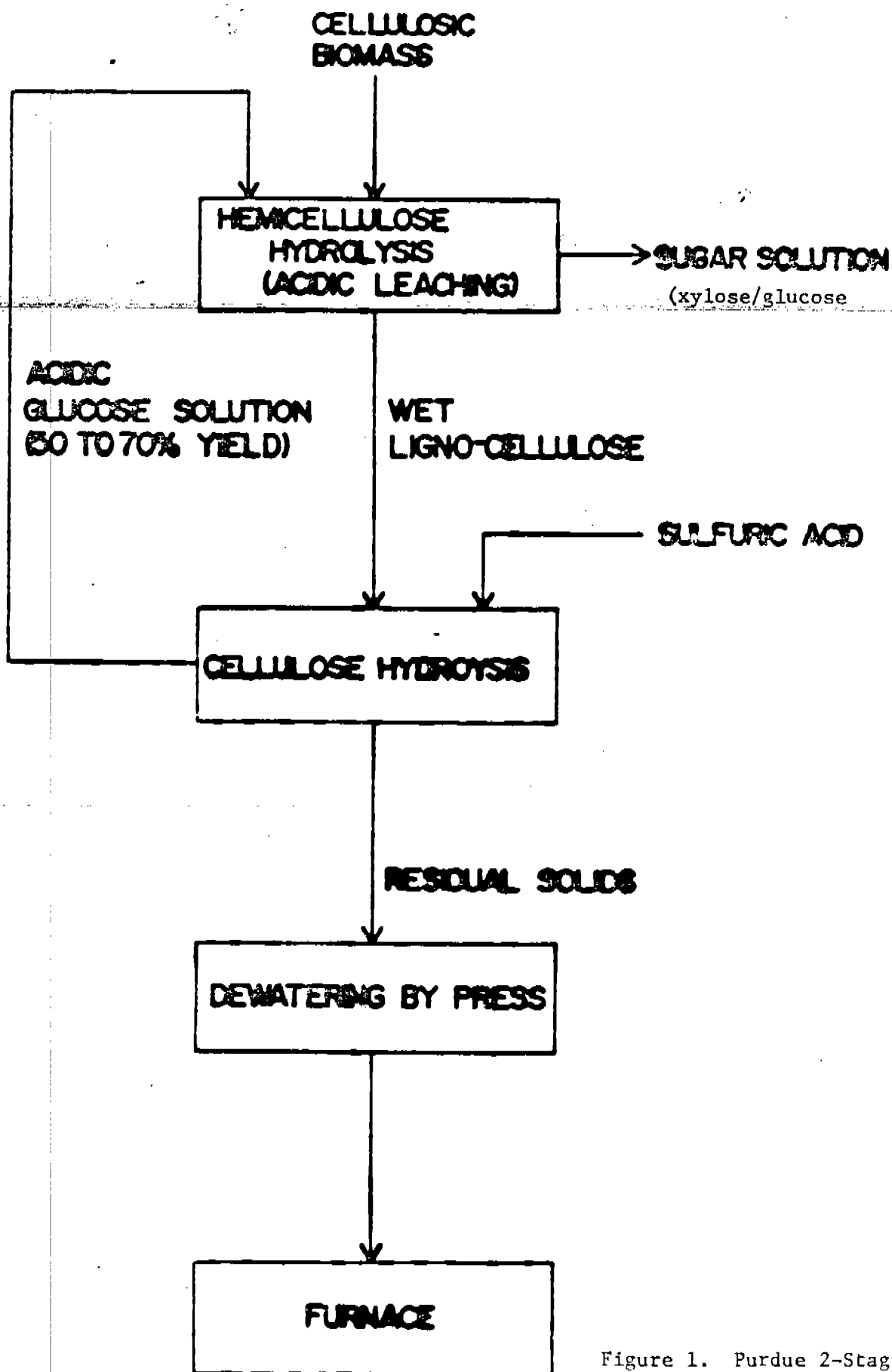
Xylose isomerase which is more commonly known as glucose isomerase becomes unstable in the presence of calcium ions. Lime neutralization of sulfuric acid is therefore not a totally acceptable processing method if the xylose is intended to be converted to ethanol via xylulose. Removal of the acid by a solid adsorbent would be a useful alternative method.

A class of solid polymeric amine (PA) has been synthesized. They can adsorb a rather large amount of mineral acids as well as organic acids.

II. EXPERIMENTAL DESCRIPTION

Figure 2 shows the experimental arrangement of the column system used to determine adsorption/desorption properties. A Milton Roy model NSI-33R pump provides a steady flow rate. A 5 microliter pulse of the sample solution was created by using a Rheodyne model 70-10 loop-injection valve positioned between an Ace 1x30 cm column and a Waters R-401 differential refractometer. The elution volume was measured by collecting the column effluent in a graduated cylinder. The column temperature was maintained by a Haake model FE water bath pump. An Instrumentation Specialties model 1200 fraction collector was used to collect the column effluent for further analysis.

A dilute aqueous solution containing 1-10 weight percent of desired material is transferred to the adsorption zone downward. The particle size of the resin in fixed-bed is not critical, the smaller particle size being preferred because the efficiency of sorption is related in part to the available surface area of the resin. In general, an average particle size from about 20 to 300 mesh, and preferably, from about 40 to 150 mesh provides good results. The quantities of resin used can vary widely if factors such as the concentration of desired material in the feed, the volume of the feed and



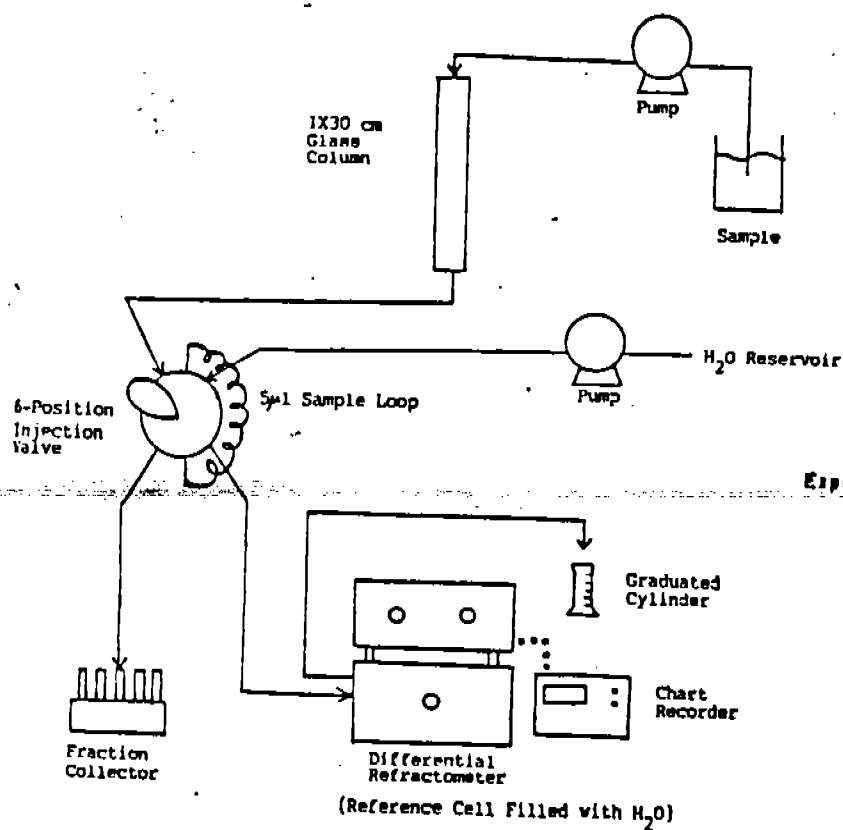


Figure 2.

Experimental apparatus for column systems.

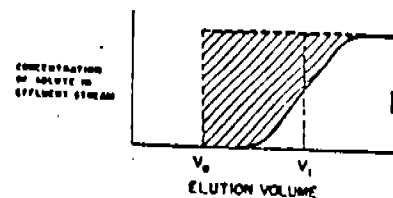
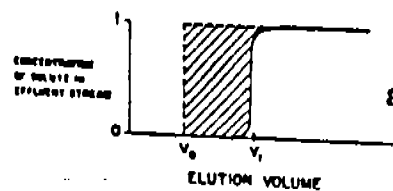
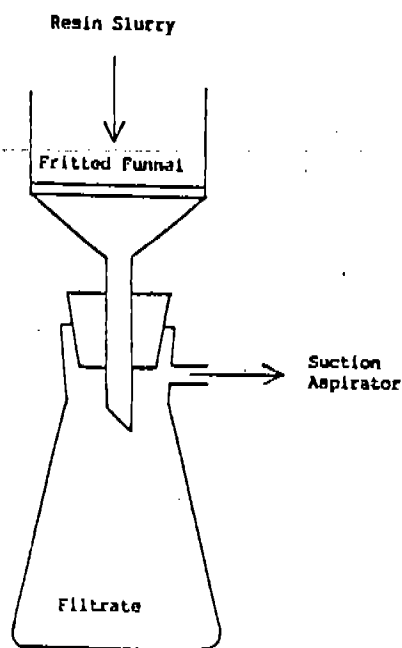


Figure 4.

Adsorption breakthrough curve for a single component (a) without dispersion, (b) with dispersion.

Figure 3. Apparatus for suction filtration.

its flow rate, the temperatures of the feed and sorption zone, contact time of the feed with the resin, and other similar factors are taken into account.

The cross-linked PA resin particles are insoluble in all solvents; their use simplified product isolation and reduces contamination of effluent streams. The PA hard granular particles resist attrition due to abrasion and osmotic shock. This in addition to its good temperature stability allows the resin to be recycled many times.

The capacity of cross-linked PA resins to adsorb desired material from a dilute aqueous solution was tested. The adsorption isotherm was determined over the concentration range of 1% to 10% by weight. The experiments were conducted by equilibrating 1.0 g portions of resin with 10 ml volumes of aqueous desired material of various concentrations. The mixtures were allowed to stand for 20 hours with occasional stirring. Analysis was made by introducing the supernatant liquid into a liquid chromatographic apparatus. The relative amount of desired material adsorbed was determined from the difference between the initial amount before adsorption and the final amount. The following mass balance equations demonstrate the calculation method for adsorbability.

$$\rho_i V_i C_i = \rho_f V_f C_f + M X \quad (1)$$

$$X = \frac{\rho_i V_i C_i - \rho_f V_f C_f}{M} \quad (2)$$

where

C_i = the initial concentration of solution (% by wt.)

C_f = the final concentration of solution (% by wt.)

M = the weight of dry resin (g)

V_i = the initial volume of solution before adsorption (ml)

V_f = the final volume of solution after adsorption (ml)

X = the weight of desired material adsorbed per gram of dry resin (g/g)

ρ_i = the initial density of solution (g/ml)

ρ_f = the final density of solution (g/ml)

Since the resin is porous, swelling may be expected and the amount of solution adsorbed by a gram of dry resin has to be determined. Several approaches can be

used to measure the final solution volume after adsorption. Therefore, the amount of solution adsorbed by a gram of dry resin will be known from the difference of solution amounts before and after adsorption.

The first approach is to use a centrifuging apparatus to separate the resins from the surrounding solution. The second method is to utilize suction filtration so that the solution among particles can be removed (see Figure 3). Before filtration was applied, the fritted funnel and the empty flask were weighed. After suction filtration was done, the fritted funnel with wet resin and the flask with filtrate were reweighed. The wet resin was put into an oven and dried at 90°C for two days before the dry resin was weighed. From the weight difference between wet resin and dry resin, the amount of solution adsorbed per gram of dry resin used can be calculated. Furthermore, this uptake value may be checked by the weight difference between the initial solution and the final filtrate.

The third approach is based on frontal analysis in order to evaluate the column adsorption capacity. The procedure involves packing the resin in a column which is initially filled with pure solvent. A solution containing one or more solutes is continuously fed into the column. The total solute concentration of the effluent from the column is measured and plotted as a function of the elution volume. An example of a breakthrough curve is given in Figure 4. The shaded volume collected between V_1 and V_0 in this figure is the amount of solution which has been stripped of its solute. When the concentration of solute in the effluent levels off and equals the solute concentration being introduced into the column, the amount of the adsorbed material will be in equilibrium with the concentration in the eluate. The adsorption isotherm can be plotted from a series of breakthrough curves produced by using different inlet concentrations.

With the apparatus set up in Figure 2, the dead volume and elution volume were determined. The resin adsorption capacity of desired material can be calculated by the following equation.

$$X = \frac{C_f \rho_f (V_1 - V_0)}{M} \quad (3)$$

where

C_f = the feed concentration (% by wt.)

M = the weight of the dry resin packed into column (g)

V_o = the deal volume (ml)

V_1 = the elution volume (ml)

~~X = the weight of desired material adsorbed per gram of dry resin used (g/g)~~

ρ_f = the density of feed solution (g/ml)

The comparison of the resin capacities between a batch and a column system was made. The agreement of resin adsorption capacities offers an assurance of the determination for the solution amount adsorbed by per gram of dry resin.

III. RESULTS

A. Adsorption Capacity of PA Resins

1. *Mineral Acids.* The adsorption isotherm of hydrochloric acid has been determined. This Langmuir-type isotherm is shown in Figure 5. The equilibrium constants K_1 and K_2 are determined as 1.170 and 3.331, respectively. The equation of the hydrochloric acid adsorption equilibrium isotherm is

$$\frac{X}{M} = \frac{1.170 C}{1. + 3.331 C}$$

The effect of temperature on hydrochloric acid adsorption has been studied. As the temperature goes up, the adsorbability increases (see Figure 6). The adsorption isotherm for sulfuric acid by the PA resins is shown in Figure 7.

2. *Organic Acid.* As shown in Figure 8, lactic acid can also be readily adsorbed by PA resins. The results in Figure 9 also indicate that the adsorbed lactic acid can be recovered by elution with sulfuric acid.

IV. DISCUSSION AND FUTURE WORK

This project started out as an effort for recycling sulfuric acid from acid hydrolyzate of cellulosics. While we are completely successful in removing sulfuric acid from the sugar solution; the recovery of the adsorbed sulfuric acid from the polymeric amine

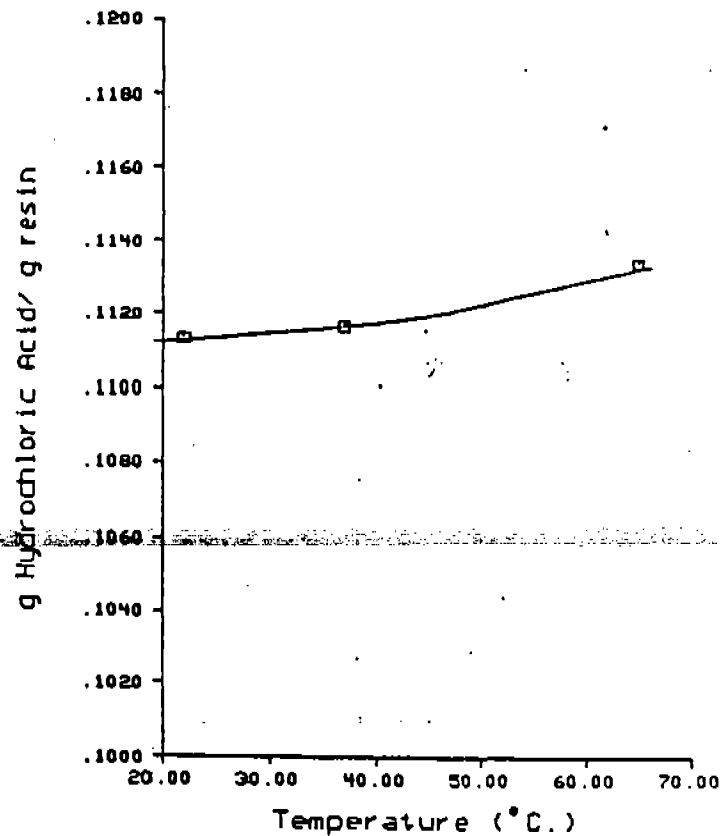
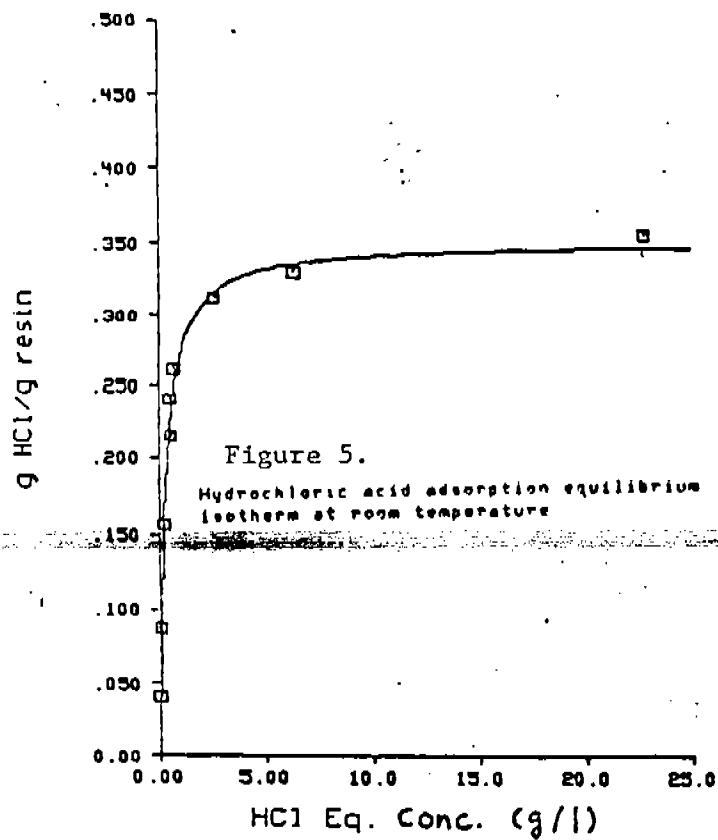
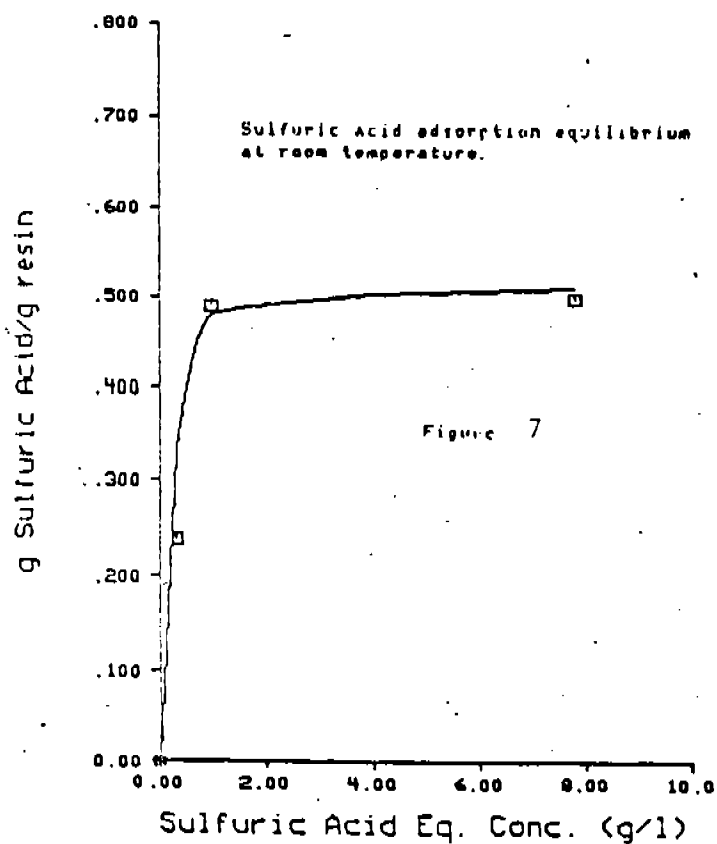


Figure 6 Effect of temperature on hydrochloric acid adsorption.



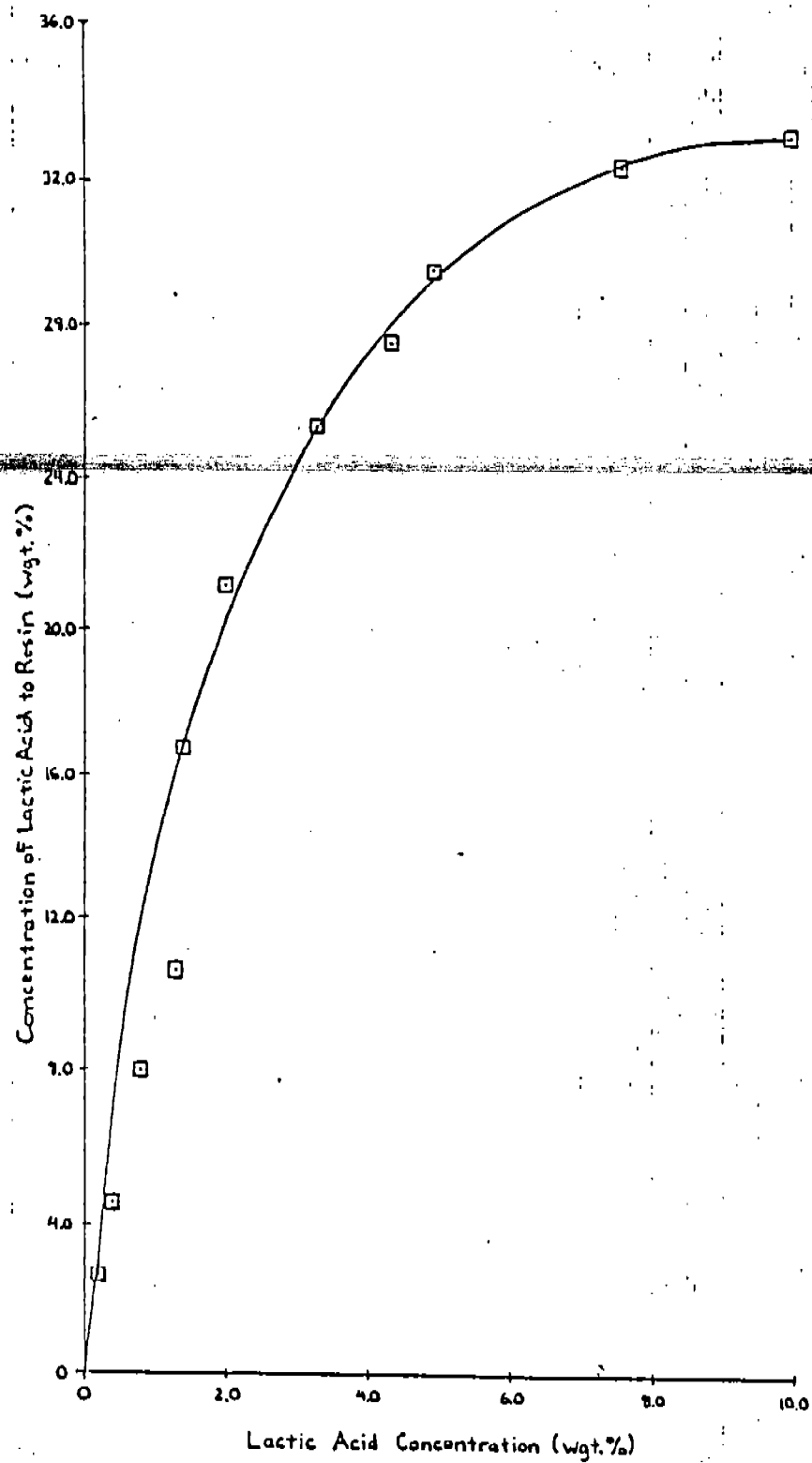


Figure 8: Absorption Equilibrium Isotherm for Lactic Acid

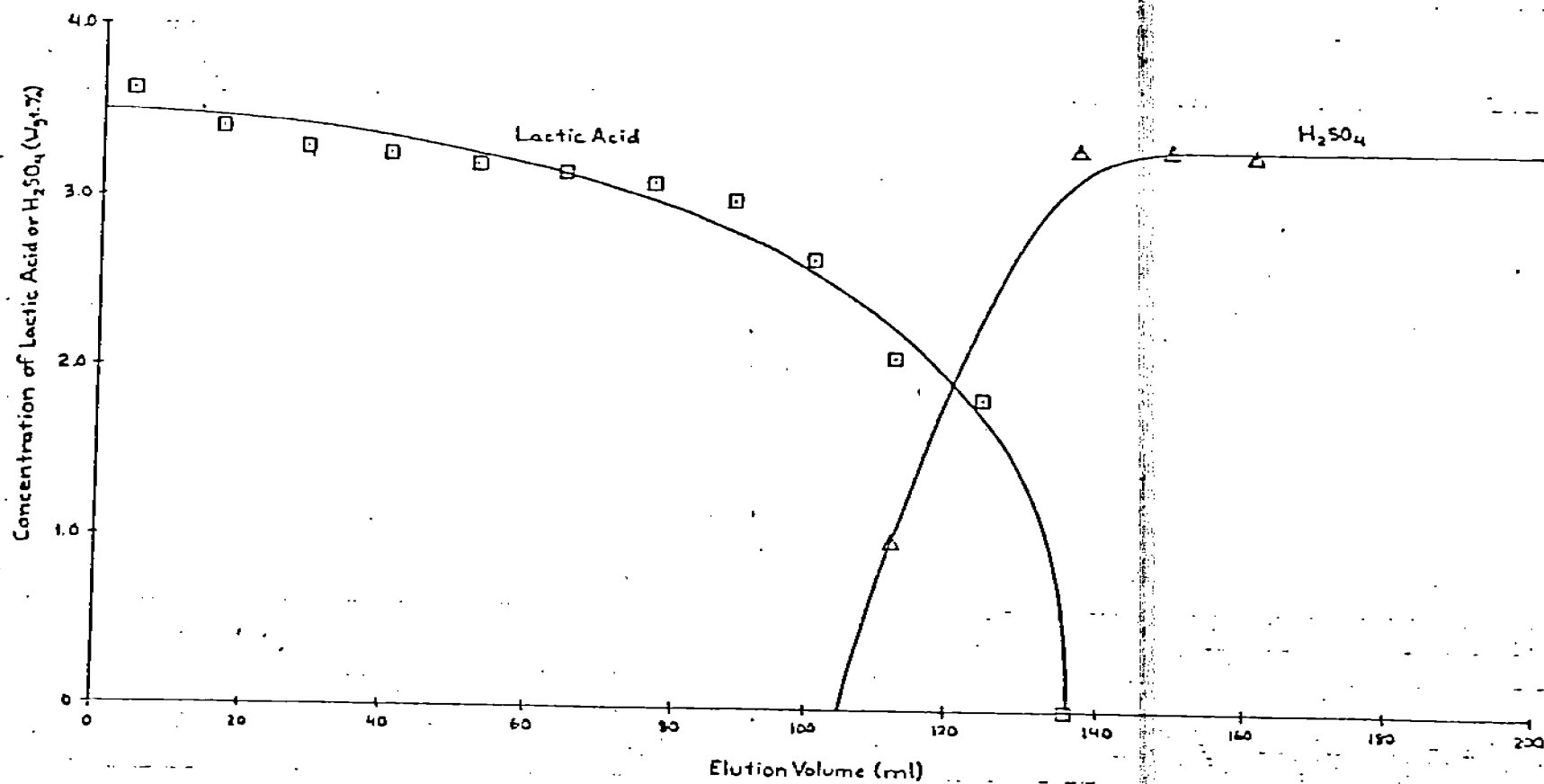


Figure 9: Desorption Plot for Lactic Acid Eluted with Sulfuric Acid

resin particles was found to be difficult. To regenerate the resin, we still need to use an alkaline to neutralize the adsorbed sulfuric acid; this will *not* reduce the acid and the chemical cost for the overall process of acid hydrolysis of cellulose as a part of the ethanol fuel research effort.

The solid PA resin does remove sulfuric acid thus eliminating the need of adding lime directly to the xylose/glucose solution. This will benefit the stability of xylose isomerase, which is apparently of current interest to SERI in its overall ethanol program.

If financial support is made available, we will be able to carry out future work to quantify the benefit of PA in prolonging the isomerase activity half life in a coupled enzymatic isomerization and yeast fermentation process for producing ethanol from xylose in the acid hydrolyzate.

V. REFERENCES

- Chiang, L. C., Gong, C. S., Chen, L. F., and Tsao, G. T. 1981. "D-Xylulose Fermentation to Ethanol by *Saccharomyces cerevisiae*," *Appl. Environ. Microbiol.* 42:284.
- Gong, C. S., Chen, L. F., Flickinger, M. C., and Tsao, G. T. 1984. "Production of Ethanol by Yeast Using Xylose," U.S. Patent 4,490,468.
- Rodriguez, G. 1983. "Studies on the Simultaneous Enzymatic Isomerization and Yeast Fermentation of D-Xylose," Ph.D. Thesis, Purdue University, December.